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(54) Title: HOMOGENEOUS ELECTRO-VISCOUS FLUIDS

(57) Abrégé/Abstract:
Homogeneous, electro-viscous fluids are provided which comprise aluminium soaps based on products obtained by reacting one or more polycarboxylic acid(s) or the anhydrides or semi-esters thereof with reactive aluminium compounds. The aforesaid fluids manifest a high electro-rheological effect and are completely homogeneous.

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Abstract

Homogeneous, electro-viscous fluids are provided which comprise aluminium soaps based on products obtained by reacting one or more polycarboxylic acid(s) or the anhydrides or semi-esters thereof with reactive aluminium compounds. The aforesaid fluids manifest a high electro-rheological effect and are completely homogeneous.

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Homogeneous Electro-Viscous Fluids

This invention relates to homogeneous electro-viscous fluids (EVF).

Electro-viscous fluids have been known for some time in the form of finely divided, hydrophilic solids dispersed in hydrophobic fluids. The special features of such fluids are that their flow characteristics and, thus, their viscosities can be changed within a large range by subjection to an electrical field, thereby providing a great variety of applications. Electro-viscous fluids are particularly intended for use in the field of industrial and vehicle hydraulics, e.g. for machine and engine bearings or dampers, for positioning work-pieces, for levelling out, cushioning and damping vehicles, for hydrodynamic power transmission and automatic clutches.

The compositions of known electro-viscous fluids for said applications may be rather different. Usually, electro-viscous fluids comprise three components: a dispersed phase containing silicates, zeolites, titanates, semiconductors, polysaccharides or organic polymers; an electrical, non-conducting hydrophobic fluid as liquid phase; a dispersant. In DE 35 36 934 A1 electro-viscous fluids have been described the dispersed phase of which comprises aluminium silicates having a water content of from 1 to 25 wt.-% and an Al/Si atomic ratio on its surface of between 0.15 and 0.80.

However, since all heretofore known electro-viscous fluids are emulsions they have the disadvantage of requiring a considerable amount of additional dispersive components to reduce the material-related tendency to sedimentation. Therefore, for use in modern hydraulic aggregates most of the known products have proved to be unsatisfactory, especially when used over long periods. In particular, conventional dispersions manifest techno-hydraulic disadvantages some of which are listed in the following:

- tendency to very high abrasion
- evaporation of water of crystallisation
- nonfilterability (no separation of foreign matter)

- presence of components which are critical under toxicological and safety aspects
- incompatibilities with elastomeric sealants.

Furthermore, it is known that a great number of high-polar fluids, too, change their flow characteristics in a high-voltage field. But since these effects are only weak, no technical use can be made thereof.

Therefore, it is the object of this invention to provide homogeneous electro-viscous fluids which comply with the technical requirements made on a modern industrial hydraulic fluid and which do not have the foregoing disadvantages, but rather manifest a high electro-viscous effect.

According to the present invention, the problem is solved by providing electro-viscous fluids comprising aluminium soaps prepared by reacting

one or more saturated and/or unsaturated monomeric, oligomeric and/or polymeric C_3 to C_{32} polycarboxylic acid(s) having one or more carboxyl group(s), the anhydrides and/or semi-esters thereof the alcohol component(s) of which is (are) linear or branched monohydric or polyhydric C_1 to C_{12} alcohols and/or the oligomers thereof,

with one or more of the following reactive aluminium compound(s): aluminium alkyls, aluminium oxoalkyls, aluminium hydroxycarboxylates, aluminium oxocarboxylates, aluminium oxoalcoholates, aluminium alkoxycarboxylates, aluminium oxides and/or aluminium oxyhydrates.

It is preferred that the reactive aluminium compounds be

aluminium alkyls and aluminium oxoalkyls having linear or branched C_1 to C_6 alkyl residues;

aluminium hydroxycarboxylates and aluminium oxocarboxylates having linear or branched aliphatic or unsaturated C_2 or C_{30} carboxylic acids;

aluminium oxoalcoholates having linear or branched aliphatic C_1 to C_6 alcohols;

aluminium alkoxycarboxylates having linear or branched aliphatic C_1 to C_6 alcohols and linear or branched aliphatic or unsaturated C_2 to C_{30} carboxylic acids;

and aluminium oxides and aluminium oxyhydrates of the general formula $Al_2O_3 \cdot nH_2O$ (n = 0 bis 6).

It was surprisingly found that by doping with aluminium a great electro-rheological effect is attained. The resultant products are completely homogeneous.

The aluminium soaps used according to this invention are the products obtained by the reaction of polycarboxylic acids, anhydrides or semi-esters with the active aluminium compounds, all or part of the valences of the aluminium having been converted.

It is preferred that the electro-viscous fluids according to the invention comprise the following components:

component (a): 2 to 50 wt.-%, preferably 5 to 40 wt.-%, particularly 10 to 35 wt.-% of the aluminium soap, in homogeneous solution with

component (b): 50 to 98 wt.-%, preferably 60 to 95 wt.-%, particularly 65 to 90 wt.-% of a conventional hydraulic base fluid, and additionally

component (c): 0 to 10 wt.-%, preferably 0 to 5 wt.-%, particularly 0.1 to 2 wt.-% of soluble hydraulic additives known as such,

each referring to the total composition.

Component (a) consists of oligomeric complex aluminium soaps based on reaction adducts of polycarboxylic acids or olefin carboxylic acids, the anhydrides, semi-esters or oligomers thereof with the active aluminium compounds. Saponification takes place, wholly or in part, for example by controlled partial hydrolysis yielding hydroxyl soap structures.

By polycarboxylic acid are meant carboxylic acids obtained by reaction of unsaturated carboxylic acids with each other or with olefins. The oligomers thereof used are compounds consisting of 2 to 10 units, preferably 2 to 6 units.

As alcohol components of the polycarboxylic acid semi-esters linear or branched monohydric or polyhydric alcohols are used. It has proved to be advantageous if the carbon number is determined by the base fluid in order to ensure that the corresponding reaction products are soluble.

Examples of component (a) are partial ester/aluminium soap adducts based on alkenyl succinic anhydrides, particularly n-hexenyl succinic anhydrides, diisobutenyl succinic anhydrides, tetrapropenyl succinic anhydrides, dodecenyl succinic anhydrides and polyisobutenyl succinic anhydrides.

Also suitable are e.g. olefin addition products of itaconic, citraconic and mesaconic acid.

Furthermore, copolymerisates of unsaturated carboxylic acids, e.g. of maleic, fumaric, acrylic or methacrylic acid are appropriate. Polyesters containing carboxyl groups which are based on saturated or aromatic dicarboxylic acids, such as adipic acid or phthalic acid, are also suitable.

Component (b), the hydraulic base fluid, is a basically non-conducting fluid capable for homogeneously dissolving carboxylic acid aluminum salts, or the reaction product of the aluminum compound with the carboxylic acid compound, to be used as the hydraulic base fluid component. Component (b) comprises hydraulic media, such as conventional mineral oil selective raffinates, hydrocracking products, hydrogenates, poly-alpha-olefins or synthetic esters. "Base fluid" is meant to indicate that component (b) is the main part or ingredient to which other components are added.

The viscosities of the aforesaid fluids are selected in dependence on the intended use of the end product.

Examples of component (b) are:

Spindle oil raffinate 6/20 of DEA, Hamburg

Kinematic viscosity ($40^{o}C$); 4.2 mm^2/s

Density ($15^{o}C$): 840 kg/m^3

Solvent raffinate SN 45 of DEA, Hamburg
Kinematic viscosity (40 °C): 6.5 mm^2/s
Density (15 °C): 842 kg/m^3

Hydrocracking product VHVI-light of DEA, Hamburg
Kinematic viscosity (40 °C): 30.4 mm^2/s
Density (15 °C): 854 kg/m^3

Hitec 162, PAO of Ethyl, St. Louis
Kinematic viscosity (40 °C): 5.0 mm^2/s
Density (15 °C): 800 kg/m^3

Priolube 3958 of Unichema, Gouda
Kinematic viscosity (40 °C): 10.5 mm^2/s
Density (15 °C): 921 kg/m^3

Component (c) comprises customary hydraulic additives for optimising the hydraulic product characteristics, such as wear resistance, resistance to ageing, friction characteristics, resistance to foaming, corrosion resistance and low-temperature characteristics.

Examples of component (c) are:

Additin RC 3212 of Rhein-Chemie, Mannheim
2-Ethylhexyl-Zn-dithiophosphate

Irganox L 107 of Ciba-Geigy, Basel
2,6-di-tert-butylphenol

Viscoplex 1-300 of Röhm, Darmstadt
Polymethacrylate, 70 % solution in neutral raffinate

In a preferred embodiment of the process for producing electroviscous fluids the dilute olefin carboxylic acid semi-ester is placed into the vessel and blended with the aluminium carrier component in the absence of moisture. After the chemical reaction is complete, a sufficient amount of component (b) is added to adjust

the viscosity to the rated value, and component (c) is added as required.

In a voltage field of from about 500 V/mm field strength, the fluids thus prepared show a significant increase in viscosity as the field strength increases. Optimum response is reached between 3 and 8 kV/mm field strength, the aluminium content being preferably 0.1 to 0.5 %. The initial viscosity of the electro-viscous fluid may be in the range of from 15 to 6,000 mPa·s at 40 °C.

Embodiments of the Invention

In the embodiments described in the following, Example 1 is based on a polycarboxylic acid not reacted with an active aluminium compound. The acid proved to be ineffective.

Examples 2 to 4 describe reaction products of the invention. The corresponding electro-rheological measurement results are shown in the Table hereinbelow.

Example 1 (Comparison)

100 grams of a tetrapropenyl succinic acid semi-ester having the following characteristics

Density (15 °C)	985	kg/m^3
Kinematic viscosity (40 °C)	1,750	mm^2/s
Viscosity (100 °C)	31	mm^2/s
Flash point P.M.	175	°C
Mineral oil content	37	wt.-%
Acid number	144	mg KOH/g
Hydroxyl number	43	mg KOH/g

were diluted with 100 g of a naphthenic mineral oil cut.

0.1 % of a commercially available demulsifier and
0.1 % of a commercially available defoamer
were added to this mixture.

The final mixture had a viscosity of 39 mm^2/s at 40 °C and an acid number of 72 mg KOH/g.

When testing the aforesaid mixture in a high-voltage rotary rheometer, no increase in yield stress was detectable up to a field strength of 8 KV/mm at a shear rate of D = 1/100.

Example 2

Reaction of an Aluminium Oxoalkyl

50 grams of the tetrapropenyl succinic acid semi-ester as described in Example 1 were dissolved in 150 ml of toluene, cooled to -30 °C and made inert. 33 ml of a 10 % solution of methyl aluminium oxide (product of Witco company) were injected with a syringe. The temperature was gradually increased to room temperature whereby gas was formed. After the evolution of gas was complete, the temperature was raised and maintained at 80 °C for 2 hours to complete reaction. The toluene was eliminated on the rotary evaporator and 50 ml of a naphthenic white oil were added as hydraulic base oil. The product then was examined.

Example 3

Reaction of an Aluminium Oxocarboxylate

A mixture comprised of 10 g of the tetrapropenyl succinic acid semi-ester described in Example 1, 6 g of aluminium-oxo-2-ethylhexanoate (DOROX® D 490 of CONDEA Chemie), 15 g of 2-ethylhexanoic acid and 130 g of naphthenic white oil as hydraulic base oil was heated to 120 °C during one hour. After cooling the product was examined.

Example 4

Reaction of an Aluminium Oxide Hydrate

A mixture comprised of 10 g of the tetrapropenyl succinic acid semi-ester described in Example 1, 2.5 g of aluminium oxide hydrate (Disperal® of CONDEA Chemie), 15 g of pelargonic acid and 130 g of naphthenic white oil as hydraulic base oil was heated to 120 °C during one hour. Filtration by means of a press filter was performed at 80 - 100 °C. After cooling the product was examined.

TABLE

ELECTRORHEOLOGICAL MEASUREMENTS

	Tension U kV	Power I mA	Shear Rate 1/s	Yield Stress Pa	ERF Yield Stress Pa	ERF Factor
Example 2	-	-	600	103	-	-
	1.0	0.08	600	116	13	1.12
	2.0	0.12	600	142	39	1.37
	4.0	0.24	600	213	110	2.06
	6.0	0.32	600	341	236	3.31
	8.0	0.42	600	547	444	5.30
Example 3	-	-	17.7	27	-	-
	1.0	0.00	17.7	36	9	1.33
	2.0	0.00	17.7	53	27	2.00
	3.0	0.01	17.7	82	56	3.09
	4.0	0.01	17.7	111	84	4.17
Example 4	-	-	17.7	25	-	-
	1.0	0.00	17.7	34	9	1.36
	2.0	0.01	17.7	50	25	2.00
	3.0	0.01	17.7	74	49	2.96
	4.0	0.02	17.7	103	78	4.12

CLAIMS:

1. A homogeneous electro-viscous fluid comprising an aluminium soap produced by reacting at least one member selected from the group consisting of saturated and unsaturated monomeric, oligomeric and polymeric C_3 to C_{32} polycarboxylic acids having one or more carboxylic group, the anhydrides and semi-esters thereof which alcohol component comprise linear and branched, monohydric and polyhydric C_1 to C_{12} alcohols and oligomers thereof with one or more reactive aluminium compounds selected from aluminium alkyls, aluminium oxoalkyls, aluminium hydrocarboxylates, aluminum oxocarboxylates, aluminium oxoalcoholates, aluminium alkoxycarboxylates, aluminum oxides and aluminium oxhydrates.

2. The electro-viscous fluid of claim 1, comprising an aluminium alkyl or aluminium oxoalkyl comprising a linear or branched alkyl residue of 1 to 6 carbon atoms.

3. The electro-viscous fluid of claim 1, comprising an aluminium hydroxycarboxylate or aluminium oxocarboxylate comprising a residue of a linear or branched aliphatic or unsaturated carboxylic acid of 2 to 30 carbon atoms.

4. The electro-viscous fluid of claim 1, comprising an aluminium oxoalcoholate comprising an alcohol residue of 1 to 6 carbon atoms.

5. The electro-viscous fluid of claim 1, comprising an aluminium alkoxycarboxylate comprising a residue of a linear or branched aliphatic alcohol of 1 to 6 carbon atoms or of a linear or branched aliphatic or unsaturated carboxylic acid of 2 to 30 carbon atoms.

6. The electro-viscous fluid of claim 1, comprising an aluminium oxide or an aluminium oxyhydrate of the general formula $Al_2O_3 \cdot nH_2O$, where n = 0 to 6.

7. The electro-viscous fluid of any one of claims 1 to 6, comprising a polycarboxylic acid, anhydride or semi-ester thereof comprising 3 to 18 carbon atoms.

8. The electro-viscous fluid of any one of claims 1 to 6, comprising a polycarboxylic acid, anhydride or semi-ester thereof comprising 12 to 18 carbon atoms.

9. The electro-viscous fluid of any one of claims 1 to 6, comprising an alkenyl succinic acid or semi-ester thereof comprising 5 to 18 carbon atoms.

10. The electro-viscous fluid of any one of claims 1 to 6, comprising an alkenyl succinic acid or semi-ester thereof comprising 12 to 18 carbon atoms.

11. The electro-viscous fluid of any one of claims 1 to 10, wherein, in the reaction producing the aluminium soap, all or part of the valences of the aluminium have been converted.

12. The electro-viscous fluid according to any one of claims 1 to 6, wherein the one or more polycarboxylic acid, anhydride, or semi-ester thereof comprises one or more free OH groups.

13. The electro-viscous fluid of claim 12, wherein the semi-ester of the one or more polycarboxylic acid comprises one or more free OH groups.

14. The electro-viscous fluid according to any one of claims 1 to 10, wherein the alcohol component(s) of the

semi-ester is (are) comprised of di- to tetrahydric alcohols with 1 to 6 carbon atoms, or an oligomer thereof.

15. The electro-viscous fluid according to any one of claims 1 to 14, wherein the alcohol component(s) of the semi-ester is (are) comprised of di- to tetrahydric alcohols with 2 to 5 carbon atoms, or an oligomer thereof.

16. The electro-viscous fluid according to any one of claims 1 to 15, which is comprised of:

(a) 2 to 50 wt.-% of the aluminium soap in homogeneous solution with

(b) 50 to 98 wt.-% of a hydraulic base fluid, each percentage based on the total weight of the composition.

17. The electro-viscous fluid according to claim 16, which additionally comprises:

(c) up to 10 wt.-% of soluble hydraulic oil additives known per se, based on the total weight of the composition.

18. The electro-viscous fluid according to any one of claims 1 to 15, which is comprised of:

(a) 5 to 40 wt.-% of the aluminium soap in homogeneous solution with

(b) 60 to 95 wt.-% of a hydraulic base fluid, each percentage based on the total weight of the composition.

19. The electro-viscous fluid according to claim 18, which additionally comprises:

(c) up to 5 wt.-% of soluble hydraulic oil additives known per se, based upon the total weight of the composition.

20. The electro-viscous fluid according to any one of claims 1 to 15, which is comprised of:

(a) 10 to 35 wt.-% of the aluminium soap in homogeneous solution with

(b) 65 to 90 wt.-% of a hydraulic base fluid, each percentage based on the total weight of the composition.

21. The electro-viscous fluid according to claim 20, which additionally comprises:

(c) up to 2 wt.-% of soluble hydraulic oil additives known per se, based upon the total weight of the composition.

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